

# (12) UK Patent Application (19) GB (11) 2 280 183 (13) A

(43) Date of A Publication 25.01.1995

(21) Application No 9315052.2

(22) Date of Filing 20.07.1993

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(51) INT CL<sup>8</sup>

C07D 307/89 209/48, C08G 73/10

(52) UK CL (Edition N )

C2C CAA CAB CTP CTQ C1344 C1474 C213 C22Y C22O  
C25Y C25O C251 C253 C28X C30Y C31Y C314 C337  
C351 C352 C35Y C364 C369 C386 C388 C43X C50Y  
C500 C634 C645 C662 C672 C699 C761 C763 C815  
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(58) Field of Search

UK CL (Edition M ) C2C CTQ  
INT CL<sup>8</sup> C07D 307/89  
Online databases: CAS-ONLINE

(54) Production of polyetherimides

(57) The invention relates to the use of bromophthalic anhydride (BPAN) in the production of polyetherimides (PEI's).

In one aspect, BPAN is reacted with a bisphenol to form a diaryl diether dianhydride, which can be converted to a PEI by reaction with an aromatic or aliphatic diamine or their congeners.

In another aspect, BPAN is reacted with a diamine to form a dibromo-bisimide, which is then reacted with a bisphenol to form a PEI by direct displacement polymerisation.

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PRODUCTION OF POLYETHERIMIDES

This invention relates to the production of polyetherimides.

Polyetherimides (PEI's) are an important class of high temperature polymers. They are used in a wide variety of applications such as electronic packaging, electrical insulating film and composite materials for aerospace use.

A known route for the production of PEI's proceeds via diaryl diether dianhydrides. The preparation of diaryl diether dianhydrides from nitrophthalic anhydrides in a multistep synthesis has been described in US-A-3,879,428. The synthesis is also described in T. Takekoshi, J.E. Kochanowski, J.S. Manello and M.J. Webber, J. Polym Sci., Polym Chem. Ed, 1985, 23, 1759. The conversion of these dianhydride monomers to PEI's by reaction with aromatic diamine comonomers has been described by the same authors in J. Polym Sci., Polym Symp, 1986, 74, 93. The polymerisation reaction is a variation on the conventional dianhydride-diamine route to polyimides.

A complementary route to forming the PEI's by the above process is described in D.M. White et al, J. Polym Sci., Polym Chem. Ed, 1981, 19, 1635 and in US-A-3,730,946. In this alternative procedure, the nitrophthalic anhydride is first converted to a bisimide. The PEI is then formed directly by nitro displacement from the bisimide by the dianion of a bisphenol. All of the above syntheses rely on use of nitrophthalic anhydride precursors, which are relatively expensive. The multistep route to the diaryl diether dianhydrides is also complex.

Further complex multistep procedures for obtaining diaryl diether dianhydrides have been described. US-A-3,965,125 describes the reaction of halogenated phthalimides with the dianion of a bisphenol to form a bis-etherimide. Subsequent hydrolysis and cyclodehydration yield the diaryl diether dianhydride. US-A-3,956,320 describes the nitro displacement reaction of a nitrophthalonitrile by the dianion of a bisphenol. The resulting tetranitrile is converted via hydrolysis and cyclodehydration to the diaryl diether dianhydride. However, nitrophthalonitrile is also expensive as a potential starting material.

An alternative route to PEI's is described in W.T. Schwartz, High Perform Polym, 1990, 2, 189. This describes the use of 4-fluorophthalic anhydride as a precursor to diaryl diether dianhydrides via a one step route. Formation of polyimides from the dianhydrides was demonstrated. The applicability of these monomers as precursors to a range of PEI's has also been described in M. Davies, J.N. Hay and B. Woodfine, High Perform Polym, 1993, 5, 37. This further shows that the PEI's can be formed by a complementary route. In this route, the 4-fluorophthalic anhydride is first converted to the difluorobisimide, which then undergoes direct displacement polymerisation with a bisphenol to form the PEI.

In all the above routes to either dianhydrides or direct displacement polymerisation to PEI's, success is dependent on two factors. These are:

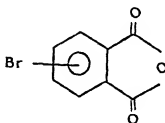
- (1) Activation of the leaving group by an appropriate electron withdrawing group. Examples of the latter include imide and nitrile groups.

- (2) The presence of a good leaving group such as nitro or fluoro.

In the halogen series, the reactivity of a halo substituent to aromatic nucleophilic displacement decreases in the order  $F^- \gg Cl^- > Br^- > I^-$  (J. March, Advanced Organic Chemistry, 3rd Ed., John Wiley, New York, (1985), p.587). This order is the opposite to that found in conventional nucleophilic displacement reactions. The critical reactions would therefore be expected to be much less facile if a fluorine leaving group were to be replaced by, for example, a bromine leaving group.

We have surprisingly found that bromophthalic anhydride (BPAN) can be converted readily to diaryl diether dianhydrides, which can then subsequently be polymerised by conventional means to PEI's. We have also found that the PEI's can be made by direct displacement polymerisation from the intermediate dibromo-bisimides derived from BPAN. The present invention thus relates to the use of BPAN in the production of PEI's and PEI precursors.

The BPAN is preferably 4-BPAN, but 3-BPAN can also be used. It has the following structure:



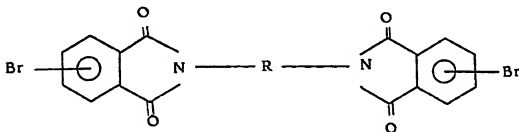
In one aspect, the invention provides a process for the production of a diaryl diether dianhydride, which comprises reacting BPAN with a bisphenol in the presence of a base in a polar aprotic solvent. The diaryl diether dianhydride can then be converted to a PEI by reaction with an aromatic or aliphatic diamine or their congeners.

In another aspect, the invention provides a process for producing a polyetherimide, which comprises reacting BPAN with a diamine or equivalent, preferably an aromatic or cycloaliphatic diamine, to form a dibromo-bisimide; and then reacting the dibromo-bisimide in the presence of a base and a polar aprotic solvent with a bisphenol to form the desired PEI by direct displacement polymerisation.

The invention thus provides new routes to PEI's

using an alternative precursor. Use of this precursor permits substantial flexibility in the choice of coreactants and polymer products. The precursor is cheaper than the precursors used in the known routes to PEI's. PEI's prepared by the routes of this invention have properties (molecular weight etc) which make them suitable for use in a wide range of applications.

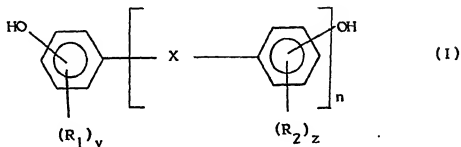
The intermediate dibromo-bisimides represent a series of novel compounds, which have the general formula:



where R is an optionally substituted aromatic, aliphatic, cycloaliphatic or heterocyclic group or combination thereof.

In principle, any bisphenol is suitable for use in the invention. These bisphenols generally have the general formula HO-Ar-OH, in which Ar is an aromatic, heterocyclic or cycloaliphatic group or combination

thereof. Some preferred bisphenols correspond to the following general formula (I):



in which

$R_1$  and  $R_2$  each independently represents alkyl or aryl, e.g.  $C_1$ - $C_4$  alkyl, and two groups  $R_1$ , or two groups  $R_2$  may be linked to complete a fused cycloaliphatic or aromatic ring, which may also be substituted;

$X$  represents a single bond, O, CO,  $SO_2$ ,  $CO_2$ , acid-containing, alkylene (preferably  $C_1$ - $C_3$  alkylene), or heterocyclic;

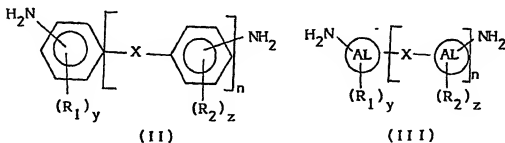
$n$  represents 0 to 5, preferably 0, 1 or 2; and

$y$  and  $z$  each independently represents 0 to 4.

Some representative examples of bisphenols, which do not constitute an exhaustive list, are shown in Table 1.

The diamines which can be used in accordance with the invention may be aliphatic, cycloaliphatic or aromatic diamines. The diamines may also be used in the

form of their equivalents, such as isocyanates, blocked isocyanates, silylated diamines and other blocked diamines. Preferred diamines correspond to the following general formulae (II) and (III):



wherein  $\text{AL} = \text{Cycloaliphatic (e.g. C}_3\text{-C}_7\text{)}$ ;

$\text{R}_1, \text{R}_2, \text{X}, n, y, z$  are defined as above;

and the amino group may be linked to a ring via a  $\text{C}_1\text{-C}_4$  alkylene group.

The diamines have the general formula  $\text{H}_2\text{N-R-NH}_2$ , where R is an aromatic, aliphatic, cycloaliphatic or heterocyclic group, and some specific, non-limiting examples of the group R are provided in Table 2.

Table 1. structures of the bisphenols used.



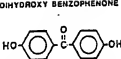
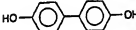
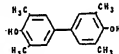
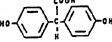
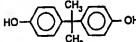
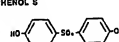
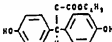
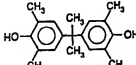
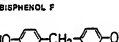

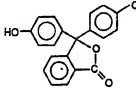
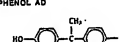

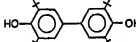
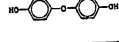

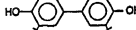
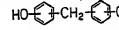

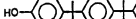
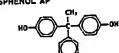

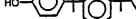
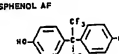

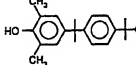
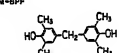


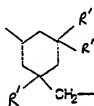
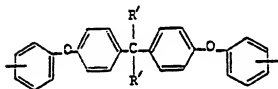
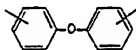
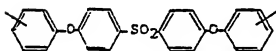
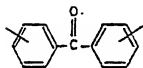
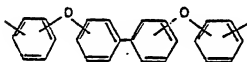
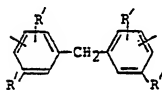
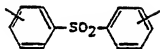
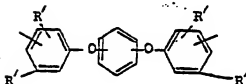
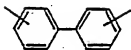
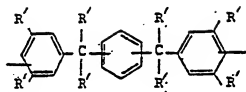
		
		
		
		
		
		
		
		
		
		
		

Table 2. Structures of the diamine R groups.



Also included are the hydrogenated cycloaliphatic variants of the above.

where R' = H or CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>.

The bases which may be used in the present invention include purely inorganic bases, strong organic bases and bases derived from organic anions. Examples of suitable inorganic bases are carbonates, hydroxides, hydrides, aluminium hydrides, borohydrides and amides of alkali and alkaline earth metals as well as some transition metals.

Examples of suitable strong organic bases are diazabicyclononene (DBN), diazabicyclooctane (DABCO), diazabicycloundecene (DBU), 'Superbase' and, in some cases, tertiary amines such as pyridine.

Examples of suitable organic anions are dimsyl, alkoxides, phenoxides, acetylides, alkyls (e.g. butyllithium) and diisopropylamide (LDA).

If appropriate, the bisphenols used in the invention may first be converted to the corresponding dianions.

The polar aprotic solvents which may be used in the invention include amides such as N-methylpyrrolidone (NMP), dimethylacetamide (DMAc) and

dimethylformamide (DMF), ethers such as tetrahydrofuran (THF), dioxane, 2-methoxyethyl ether (diglyme), triethylene glycol dimethyl ether (triglyme) and 2-ethoxyethyl ether, phosphorus-containing solvents such as hexamethylphosphoramide (HMPA), and hexamethylphosphorous triamide (HMPT), chlorinated aromatics such as chlorobenzene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, and S=O containing solvents such as sulfolane, dimethyl sulphoxide, 3-methylsulfolane, methyl phenyl sulphoxide and dimethyl sulphate.

The components of the reaction and the reaction conditions in the process according to the invention can be adapted to provide PEI's with a range of desired properties, such as a molecular weight in the range of 1,000 - 1,000,000.

An important advantage of the invention is the ability to synthesise a range of PEI's from a precursor which is readily available and cheaper than the commercially available alternatives. In comparison with the fluoride displacement route, the reactions of the invention are also safer since highly toxic and corrosive hydrogen fluoride is not produced. This is a significant

advantage both in the laboratory and in production plants. Also, in contrast to the nitro displacement route, no environmentally unfriendly nitrogen-containing by-products are produced.

The invention is illustrated by the following Examples.

Example 1

A typical diaryl diether dianhydride synthesis is as follows. 4,4'-Biphenol (20.000g; 0.1074 mol) is reacted with 4-bromophthalic anhydride (4-BPAN) (51.198g; 0.2255 mol) in the presence of sodium borohydride (9.458g; 0.25 mol) in 150g of triglyme at 185°C for 4 hours under a nitrogen atmosphere. The mixture is then allowed to cool. The solid is filtered, transferred to 1l of water, stirred and filtered. The solid is stirred again in water for 30 minutes, filtered and dried. A crude yield of 29.84g is obtained. The solid is recrystallised from 1,2,4-trichlorobenzene to give an off-white solid (26.20g; 51%). The product can be reacted with diamines or diisocyanates by any of the conventional routes described in the literature to produce a range of polyetherimides with a variety of

structures.

### Example 2

#### Part I.

Dry m-phenylenediamine (13.52g; 0.125 mol) is dissolved in dry NMP (200 ml) and 4-BPAN (56.75g; 0.250 mol) and xylene (50 ml) are added. The solution is heated to reflux and the evolved water collected in a Dean and Stark trap. After 60 min, the mixture is cooled, and the precipitated solid washed several times with methanol. The product is then dried at 150°C for 3 h, yielding an off-white powder (55.41g; 84%).

#### Part II.

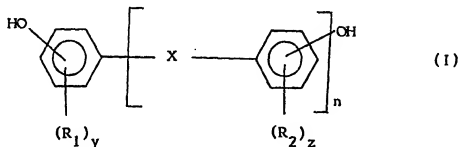
The product from Part I (6.5111g; 0.0124 mol) is dispersed in 100 ml dimethylacetamide (DMAc) at 80°C and stirred for 15 mins. m-Aminophenol (0.0793g; 0.00075 mol), bisphenol-P (4.1471g; 0.012 mol) and 1,4-diazobicyclo[2.2.2]octane (DABCO; 2.8045g; 0.025 mol) are added sequentially and residual solids washed in with 50 ml DMAc. The mixture is stirred under nitrogen and the temperature raised to reflux. After 6 h, the mixture is allowed to cool and is added slowly to 1.0 l of methanol.

The mixture is filtered, the precipitate stirred in 1.0 l of distilled water and filtered again. The solids are washed with methanol and dried at 150°C for 3 h. A cream-coloured solid (6.16g; 71%) is obtained.

CLAIMS:

1. A method of preparing a diaryl diether dianhydride, which comprises reacting bromophthalic anhydride (BPAN) with a bisphenol in the presence of a base in a polar aprotic solvent.
2. A process for preparing a polyetherimide (PEI) which comprises reacting BPAN with a bisphenol in the presence of a suitable base in a polar aprotic solvent to form a diaryl diether dianhydride, and converting the resulting diaryl diether dianhydride by reaction with an aromatic or aliphatic diamine or their congeners to form PEI.
3. A method of forming a PEI, which comprises reacting BPAN with a diamine or equivalent to form a dibromo-bisimide, and reacting the dibromo-bisimide with a bisphenol in a polar aprotic solvent in the presence of a base to form the PEI by direct displacement polymerisation.
4. A method according to any of claims 1 to 3, in which the BPAN is 4-BPAN.

5. A method according to any of claims 1 to 4, in which the bisphenol is selected from compounds having the following general formula (I):



in which

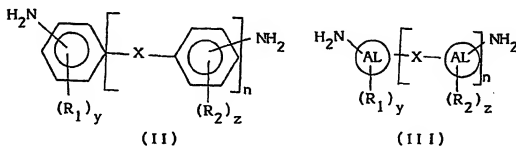
$R_1$  and  $R_2$  each independently represents alkyl or aryl, e.g.  $C_1$ - $C_6$  alkyl, and two groups  $R_1$ , or two groups  $R_2$  may be linked to complete a fused cycloaliphatic or aromatic ring, which may also be substituted;

X represents a single bond, O, CO,  $SO_2$ ,  $CO_2$ , acid-containing, alkylene (preferably  $C_1$ - $C_3$  alkylene), or heterocyclic;

n represents 0 to 5, preferably 0, 1 or 2; and

y and z each independently represents 0 to 4.

6. A method according to any of claims 1 to 5, in which the diamine is selected from compounds having the following general formulae (II) and (III):



wherein  $\textcircled{\text{AL}}$  = Cycloaliphatic (e.g.  $\text{C}_3\text{-C}_7$ );

$\text{R}_1$ ,  $\text{R}_2$ , X, n, y, z are defined as above;

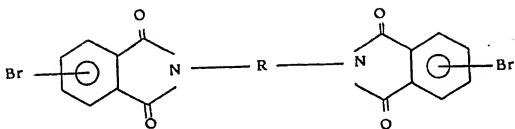
and the amino group may be linked to a ring via a  $\text{C}_1\text{-C}_4$  alkylene group.

7. A method according to any of claims 1 to 6, in which the base is an inorganic base, a strong organic base or a base derived from organic anions.

8. A method according to any of claims 1 to 7, in which the polar aprotic solvent is an amide, ether, phosphorus-containing solvent, chlorinated aromatic or  $\text{S=O}$  containing solvent.

9. Use of BPAN, preferably 4-BPAN, in the production of polyetherimides.

10. A dibromo-bisimide having the following general formula:



where R is an optionally substituted aromatic, aliphatic, cycloaliphatic or heterocyclic group or combination thereof.

11. A dibromo-bisimide according to claim 10, in which R is derived from a diamine corresponding to general formula (II) or (III) as defined in claim 6.

**Relevant Technical Fields**

- (i) UK Cl (Ed.M) C2C: CTQ  
(ii) Int Cl (Ed.5) C07D 307/89

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: CAS-ONLINE

Search Examiner  
DIANE DAVIES

Date of completion of Search  
14 OCTOBER 1994

Documents considered relevant  
following a search in respect of  
Claims :-  
1-2, 4 (IN PART)

**Categories of documents**

- X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.  
Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.  
A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	EP 0567993 A (KANEGAFUCHI KAGAKU KKK) preparation of phthalic anhydride ethers from BPAN; see in particular Reference Example 7	1-2, 4
A	CA 106:32593 & JP 61205232 A (Y KOBAYASHI) preparation of phthalic anhydride ethers from BPAN using aqueous KOH	
X	CA 94:83799 & JP 55122738 A (MITSUI KOKAI TOKKYO KOHO) preparation of phthalic anhydride ethers from BPAN using alkali metal hydroxide in a polar, aprotic solvent	

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).